Structure and environment influence in DNA conduction

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Abstract

Results for transmission through a poly(G) DNA mole-cule are presented. We show that a modification of the rise of a B-DNA form can induce a shift of the conduction channel toward the valence one. We clearly prove that deformation of the backbone of the molecule has a significant influence on hole transport. Finaly, we observe that the presence of ionic speices, such Na, near the molecule can create new conduction channels.

Keywords: DNA, transmission, conduction, molecular devices

1 Introduction

The growing interest of DNA in nanotechnology and molecular devices stems from the ability of controlled growth of nucleotide sequences and its surprising conducting properties. The mechanism and sequence dependence of conduction are not well understood. Biochemists have used photo-excitation experiments [1], [2] to point out that hole transport occurs through coherent transport at short distances [3] and long range incoherent or hopping transport at large distances [4], [5]. However, transport measurement through DNA by physicists have lead to contradictory results. Fink *et al.* [6] observed a metallic behavior in λ DNA using an electron projection microscope set-up, Kasumov *et al.* [7] observed superconducting behavior, Porath *et al* [8] observed semiconducting behavior with a poly(G)-poly(C) DNA molecule, and De Pablo *el al* [9], observed insulating behaviour using a scanning force microscope based set up.

Charge transport in DNA is a complex problem because the environment and the structure of the DNA plays a significant role in determining the energy levels of nucleotides. In fact, transformation of DNA structure has been correlated to the pH of the buffer. In this letter, we model some aspects of DNA structure and environment that influence charge transport. The system modeled here is a single poly(G) DNA molecule lying between electrodes. The transmission across the strand is computed with a Laudaüer-Buttiker formalism based on a Green's formalism [10] and a description of DNA nucleotides with an *ab initio* method in a Hartree-Fock approximation. In the following section, we will recall the basis of the method. Then we will present the results obtained for a single strand infinite poly(G) DNA molecule with various conformations and environments.

2 Theoretical background

In this study, the system modeled is a single poly(G) DNA molecule lying between electrodes. The transmission across the molecule is calculated using the Laudaüer-Buttiker formalism combined with a Green's function framework [10]. In this formalism, it is possible to model a strand (with any given sequence) connected to two semi-infinite leads as described in Ref. [11]. The transmission through the molecule has the following expression:

$$T(E) = tr\left(\Gamma_L G^r \Gamma_R G^a\right) . \qquad (1)$$

In this equation, $G^{r(a)}$ represents the retarded (advanced) Green's function and $\Gamma_{L(R)}$ the coupling between the left (right) lead and the device.

The Green's function is the solution of the following equation:

$$(ES - H - \Sigma_L - \Sigma_R) G^r = S , \qquad (2)$$

where E represents the energy of the electron, H the Hamiltonian, S the overlapping and $\Sigma_{L(R)}$ the self-energy. The overlap and Fock matrices of DNA nucleotides are obtained in the Hartree-Fock method in the local orbital basis.

3 Numerical results

3.1 Influence of the rise and twist

The existence of conformational changes *in vitro*, depending on the pH of the buffer solution, is well established. However, the conformation of dry DNA used in the transport experiments is unknown. In order to figure out the influence of conformation changes on transport properties, we investigate the influence on transmission of two of the degrees of freedom of 2 base pairs (bp) corresponding to the rise (the distance between bp) and the twist for an infinite poly(G) DNA molecule without

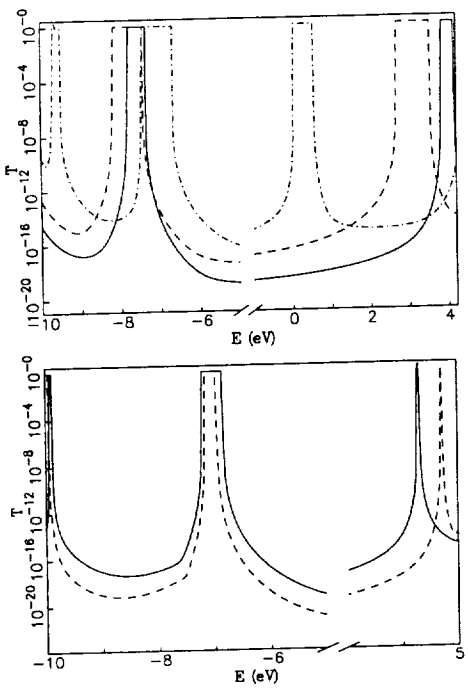

Figure 1: Transmission versus energy for different base distances of a 1 strand poly(G) DNA molecule without backbone. Top figure: The solid line corresponds to a rise of 3.38 Å, the dashed line to 3.1 Å and the dash-dotted one to 2.9 Å. Bottom figure: The solid line corresponds to a rise of 3.5 Å and the dashed one to 3.8 Å.

backbone initially in a B conformation. We will come back in the next paragraph to the possible implications of the backbone on the electronic transport properties. In this section, we have deliberately focused on the influence of the bases.

The most striking result, depicted in Fig. 1, corresponds to the variation of the transmission when the rise of an intially B form DNA is decreased. When this distance is decreased from the regular distance of 3.38 Å, the main effect is a broadening of the channels. The broadening occurs due to an increase in the hybridation between the π orbitals of the guanine. The same effect is also observed when the twist angle is decreased from its regular value of 36° (*cf* Fig. 2). However, the decrease of the rise, conversely to the twist, induces also a shift of the conduction channel. A decrease of 3.8 eV of the gap between the valence and conduction channels is observed when the distance between the bases is decreased by 0.4 Å. Conversely, an increase of the rise does not induce such drastic effect. Only a slight shift coming with a sharpening of the channel is observed. Nevertheless, even if such decrease of 0.4 Å of the base distance does not correspond to a conventional form of DNA, it represents only an increase of 0.6 eV of the total energy for a 2 bp system. These results clearly show that some

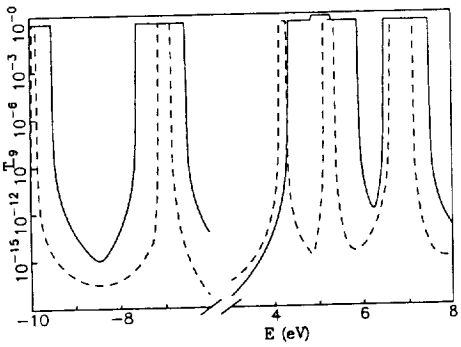

Figure 2: Transmission versus energy for different base twist angles of a 1 strand poly(G) DNA molecule without backbone. Solid line: $\Omega = 0°$, dashed line: $\Omega = 30°$.

structural modifications of DNA could deeply affect its conduction properties.

3.2 Influence of the backbone

It is only very recently that a combined theoretical and experimental study has pointed out the possible influence of the backbone with its close environement on hole transport [12]. Actually, the rather well accepted model is a strict transport by the bases without any significant influence of the backbone. This conclusion was based on the fact that it is the lowest conduction channel and the highest valence channel which are mainly involved in electron or hole transport. In the case of DNA it can easily be shown with *ab initio* calculations that, for a system of 1 or few nucleotides, the highest occupied molecular orbital (HOMO) and the lowest unocuppied one (LUMO) are mainly located on the bases. Indeed, in the present study, this conclusion has mainly been verified for infinite molecules of regular A or B DNA. Whatever the base sequence considered, we have always observed that the significant highest valence channel and lowest conduction channel are due to the bases, and that the channels due to the backbone are always at lower (higher) energies. However, for uncommon backbone structures, we have observed a non obvious exeption, which is described below.

Regular B DNA, corresponding to a tenfold right-handed helices, furanose rings puckered C_3'-*endo*, and an axial rise of 3.38 Å, may adopt several backbone structures. In this letter we will present the results obtained for 2 kinds of backbone structure. The first one, refered as regular, has been described by Arnott *et al.* [13]. The second one is obtained following the method given in Ref. [14] and differs from the regular backbone structure by a rotation of the phosphate group around the C_4-C_5 bond of the deoxyribose. Actually, we have observed, in the case of one or a few nucleotides that the HOMO and LUMO are always located on the bases. However, for the modified backbone structure, the transmission of

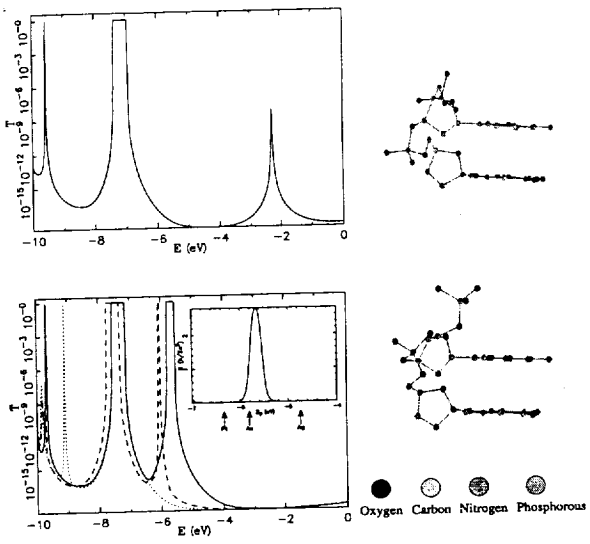

Figure 3: Left Figure: Transmission versus energy for different structures of the backbone of an infinite poly(G) DNA molecule. The top figure corresponds to regular B-DNA. The bottom one (solid and dashed lines) corresponds to two modified forms (differing by the $\widehat{POC'_3}$ angle) on which a rotation around the C_4 C_5 bond of the deoxyribose is performed. For the dotted line, the interactions between the PO_4 and the sugar are deleted. Right figure: Representation of 2 nucleotides of the regular form (top) and one of the modified form (bottom).

the infinite molecule does not depict exactly the location of the eigenvalues of a single nucleotide. Fig. 3 shows the transmission for the regular poly(G) molecule and for two different forms of the modified structure. These different forms correspond to a small deformation of the $\widehat{POC'_3}$ angle between the phosphate and the deoxyribose. On these figures, the HOMO channel is due to the backbone and not to the bases. This channel is due to a specific coupling between the phosphate group and the sugar at its 3′ end. This is clearly depicted by the dotted plot in Fig. 3 corresponding to the case where some of the interactions between the phosphate group and the sugar are set to zero. In this case the channel observed at around 6 eV disapears. Actually, this channel can be correlated to an eigenvalue of a single nucleotide occuring only when the phosphate group is bound to the 3′ end of the sugar. This result proves that the backbone can play a significant role in electronic transport when its structure is modified. Moreover, it could give some explanation of the role of the backbone in the prevention of oxidative damage to the bases.

3.3 Influence of the environment

One other parameter, which is not well characterized in most of the transport experiments on DNA, is its close environment. Actually, a DNA molecule in a saline solution is surrounded by a cloud of ionic species due to the presence of a negative charge mainly located on one oxygen of the phosphate group. The current measurements done by physicists involve either dry DNA deposited on a surface or placed in vacuum, and in these conditions, the close surroundings of the molecule is really not well known. In order to check the influence of the surroundings of the molecule on the transmission, we have introduced various ions in the close vicinity of a poly(G) B-DNA. We have done these calculations with the hypothesis that ionic species are attracted close to the molecule by electrostatic forces and stay intact after the drying process. Such behavior has already been observed and used experimentally to construct nanowires on a DNA template [15]–[17].

In all the results presented in the previous paragraphs, the oxygens of the phosphate groups, presenting a negative charge are simply passivated with hydrogens. We have performed several calculation either with hydrogens or H_3O groups and, during the self-consistent loops of the *ab initio* calculation, we have always observed, as expected, a positive ionization of the counter species. In the case of the hydrogens around a half negative charge is lost, and in the case of the H_3O one electron is lost in favour of the oxygen. However, neither with the hydrogen nor the H_3O ions are the conduction and valence channels affected. Conversely, when sodium, potassium or lithium ions are considered, new conduction channels (whith lower energy than those due to the bases) occured. The transmission for a poly(G) molecule with backbone and either H_3O^+ or Na^+ counter ions is given in Fig. 4. It can clearly be seen that the presence of the Na^+, conversely to H_3O^+, induce new LUMO channels. Actually, the PO_4^- groups of DNA act as a template leading to a helical Na wire, which is the only cause of these new channels. This has been checked by setting to zero all the matrix elements coupling the sodium and the molecule and by injecting the electrons either on the sodium or on the molecule. Moreover, we have observed that the transmission without the molecule, replacing the whole DNA molecule by OH^- ions at the location of the PO_4^- groups, lead to the occurence of the same channels. Actually, these new channels are only due to the Na wire, and the DNA molecule has no influence on them. Thus, due to its template properties for other species, great care should be taken experimentally to ensure that DNA is not contaminated by other species which could influence the transport measurement. One must notice that in the present results, conversely to those presented in Ref. [12], the influence of the Na^+ is to mainly modify the LUMO channel not the HOMO channel. Moreover, this influence is static and does not involve fluctuation between different configurations.

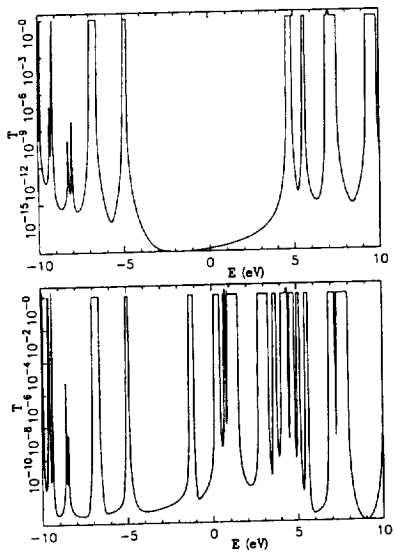

Figure 4: Transmission versus energy. Top figure: poly(G) B DNA surrounded by H_3O^+ ions (at a distance of 2.4 Å of one oxygen of the PO_4^- groups). Bottom figure: the H_3O^+ ions are replaced by Na^+ ions at the same locations.

4 Conclusion

In conclusion, we have used a Green's function formalism and an *ab initio* method to study the transmission properties of poly(G) DNA molecules. We have shown that a decrease of the distance between the bases from its regular value for B DNA lead to a shift of the lowest conduction channel toward the valence one. Moreover, we have proven that the backbone can play a significant role in electronic transport when its structure is modified. This leads to the possibility of monitoring transport in DNA by means, for example, of a STM tip. Finally, we have shown that some ionic species such as sodium could create new conduction channels (at lower energy than that of DNA) and which are independent of the molecule.

Acknowledgments

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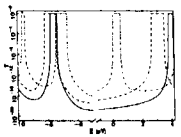
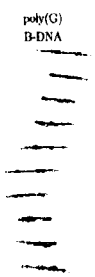
bp deformation

Rise decrease

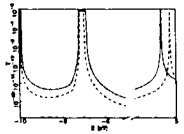


poly(G) B-DNA



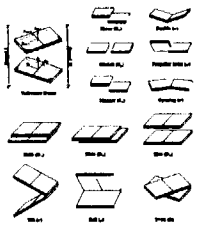
— d_{GG} = 0.338 nm
- - d_{GG} = 0.310 nm
· · · d_{GG} = 0.290 nm

Rise increase



— d_{GG} = 0.350 nm
· · · d_{GG} = 0.380 nm

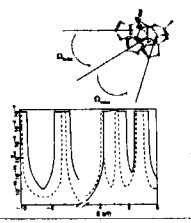
bp degrees freedom



→ 6 degrees of freedom for 1 strand

→ 12 degrees of freedom for 2 strands

Twist



— Ω = 0°
- - Ω = 30°

◇ **decreasing the rise → broadening and shift of LUMO and HOMO**

◇ decreasing the twist → only a broadening

◇ due to Π − Π interactions

◇ pH ⇒ structural modifications ⇒ variation of conductance

Structure and surroundings influence in DNA conduction

Aim: DNA based molecular devices!?

◇ ability of controlled growth

◇ non obvious transport mechanism

Sequence dependence:

hopping or tunnelling

Large range of experimental results

· **Conductor**
· DNA in UHV
· Low energy electron microscope

· **Semiconductor**
· DNA dryed
· poly(G) trapped between 2 electrodes

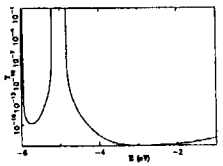
· **Insulator**
· DNA dryed on mica surface
· λ DNA scan with SFM

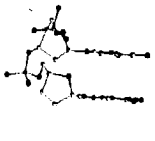
Influence of the backbone

Regular backbone structure:

◇ **HOMO channel ⇒ Guanine**

◇ 1st channel due to the bb → −9.5 eV



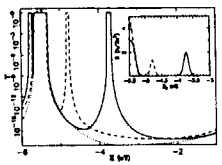


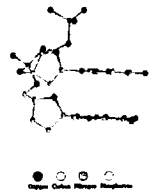
Modified backbone sturcture:

◇ Obtained by rotation of the PO_4 group

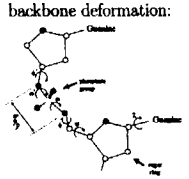
◇ **HOMO channel ⇒ backbone**

◇ Strong interaction between PO_4 and sugar





backbone deformation:



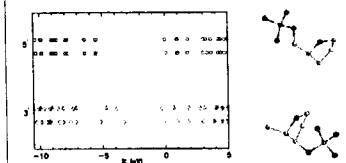
Procedure:

◇ adjust χ and ψ ⇒ 2.47 Å < $d_{O_3O_5}$ < 2.56 Å

◇ adjust ϕ and ω ⇒ $\widehat{COP} \simeq 119.3°$

◇ Eliminate unacceptable structure by means of Force Field code

DFT (B3LYP) results in single bb structures



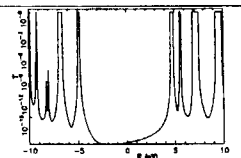
◇ **specific interactions between PO_4 and sugar at the 3′ end**

⇒ unexpected eigenvalue at higher energy than G

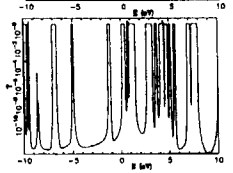
◇ not occuring if PO_4 at the 5′ end

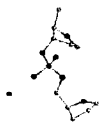
Counter ions influence on poly(G)

H_3O^+

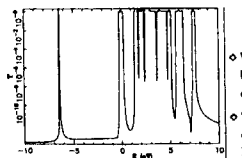


Na^+

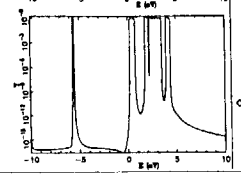




Na^+ with OH^-



K^+ with OH^-



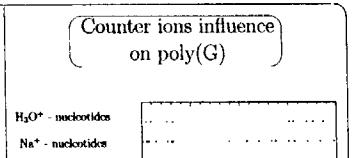
◇ With H_3O^+ counterions → both HOMO and LUMO are due to G

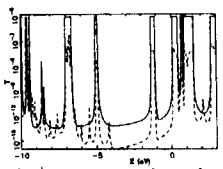
◇ **The LUMO with Na^+ counterions is due to the Na "wire"**

◇ No influence of the bases and the backbone

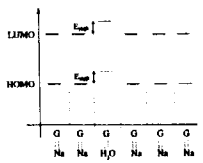
◇ **The backbone acts as a template**

◇ Same observation for the LUMO with K^+ counterions





Na^+ vacancy → mismatch

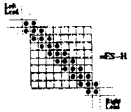


◇ H_3O^+ → local shift of eigenvalues

⇒ breaks the electronic delocalization

⇒ Channels due to the nucleotides ↓ by a factor 10^3

Formalism

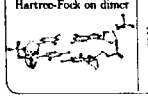


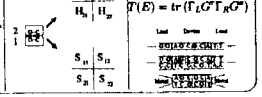
◇ Landauer-Buttiker formalism

◇ Transmission computed using a Green's function formalism

◇ Nearest neighbor bp approximations

Hartree-Fock on dimer





$T(E) = \mathrm{tr}\,(\Gamma_L G^r \Gamma_R G^a)$

Conclusions

◇ bp deformation ⇒ channel broadening and shift

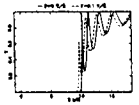
◇ bb deformation ⇒ HOMO channel due to the bb

◇ NA^+ counterions ⇒ new conduction channels

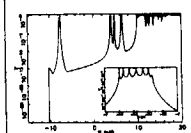
◇ Resonant tunnelling possible with given sequence

Resonant transmission

Metallic contact:



Gold|GGGGCG|Gold



◇ Metallic contacts do not modify the channels

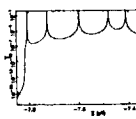
◇ **Each channels → sharp peaks**

⇒ Coming from the finite number of bases

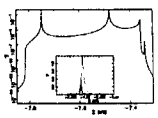
◇ Each metalic contact equivalent → $T => 1$

Sequence dependence:

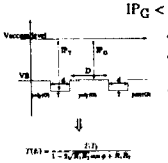
poly(G)TGGGGGGTpoly(G)



poly(G)TGGGTpoly(G)



$IP_G < IP_T$



◇ **thymines act as barriers**

◇ T→ 1, only if symmetric gates

◇ left and right coupling between T and G are slightly different T ≃ 0.94

◇ (· · · GTTGGGTG · · ·) strongly asymmetric T ≃ 0.3